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RECOVERY: A Contaminated Sediment-Water Interaction Model

Carlos E. Ruiz, Paul R. Schroeder, and Nadim M. Aziz

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RECOVERY: A Contaminated Sediment- Water Interaction Model

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Dredging Operations Technical Support

RECOVERY: A Contaminated Sediment-Water Interaction Model (ERDC/EL SR-D-00-1)

ISSUE: Toxic substances are known to associate strongly with fine-grained particulate matter. Consequently, it is not surprising that contaminants tend to accumulate in the bottom sediments of natural waters. Important questions in environmental impact assessment are to what extent do these contaminated sediments influence overlying water and how the impacts can be minimized.

RESEARCH: To more easily screen these environmental impacts, a modeling framework was designed to assess the impact of contaminated bottom sediments on surface waters and the effectiveness of capping contaminated sediments. The present model (RECOVERY) is an application and extension of frameworks developed previously. The model was verified against laboratory and field data, as well as against an analytical solution for the water and mixed sediment layers. These comparisons indicate that the model can be used as an assessment tool for the "no-action" alternative and for remediation alternatives for contaminated bottom sediments.

SUMMARY: RECOVERY is a screening-level model to assess the long-term impact of contaminated bottom sediments on surface waters. The model couples contaminated interaction between the water column and the bottom sediment, as well as between the contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the water column is well mixed. Processes incorporated in the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, and pore-water diffusion. The solution couples contaminant mass balance in the water column and in the mixed sediment layer along with diffusion and bioturbation in the deep sediment layers.

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Contents

Preface	vi
1–Introduction	1
2–Numerical Model	3
Contaminant Mass Balances	3
Solids Budget	4
Parameter Estimation	5
Numerical Solution	7
3–Verification	8
Model Verification With Analytical Solution	8
Model Verification With Laboratory Data	11
Field Verification	12
4–Conclusions	18
References	19
Appendix A: Notation	A1
SF 298	

Preface

This report describes a screening-level model (RECOVERY) used to assess the long-term impact of contaminated bottom sediments on surface waters and its application to evaluate subaqueous capping of contaminated sediment. This work was conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Research and Development Center (ERDC), Waterways Experiment Station (WES). Funding for the research was provided under the Dredging Operations Technical Support Program, U.S. Army Corps of Engineers. The project manager was Mr. Thomas R. Patin.

This report was written by Dr. Carlos E. Ruiz, Water Quality and Contaminant Modeling Branch, Environmental Processes and Effects Division, EL, Dr. Nadim M. Aziz, Clemson University, and Dr. Paul R. Schroeder, Special Projects Group, Environmental Engineering Division (EED), EL. Technical review of this report was provided by Dr. Tommy E. Myers and Dr. Mark S. Dortch, EL.

This study was conducted under the direct supervision of Mr. Norman R. Francingues, Chief, EED, and under the general supervision of Dr. John Keeley, Acting Director, EL.

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1 Introduction

Toxic substances are known to associate strongly with fine-grained particulate matter. Consequently, it is not surprising that contaminants tend to accumulate in the bottom sediments of natural waters. Important questions in environmental impact assessment are to what extent do these contaminated sediments influence overlying water, and how the impacts can be minimized.

Pollutants in bottom sediments can be released by resuspension of particles, mixing by benthic organisms, and diffusion from the sediment pore water. On the other hand, pollutants in the water column can be transferred to the sediment layer by settling and to the atmosphere by volatilization. The present paper describes a modeling framework that is designed to assess the impact of contaminated bottom sediments on surface waters. The analysis is limited to cases where the overlying water is well-mixed. In addition, the contaminant is assumed to follow reversible linear equilibrium sorption and first-order decay kinetics.

The present model (RECOVERY) is an application and extension of frameworks developed previously (Boyer et al. 1994, Chapra 1982, and Chapra and Reckhow 1983). As shown in Figure 1, the system is idealized as a well-mixed surface water layer underlain by a vertically stratified sediment column. The sediment is well-mixed horizontally but segmented vertically into a well-mixed surface layer and deep sediment. The latter, in turn, is segmented into layers with varying thicknesses, porosities, and contaminant concentrations underlain by an uncontaminated region. The discretized sediment layer configuration is useful for capping scenarios and sites where contamination occurred over a long time; thus, contamination appears layered. The specification of a mixed surface layer is included because an unconsolidated layer is often observed at the surface of sediments due to a number of processes, including bioturbation and mechanical mixing.

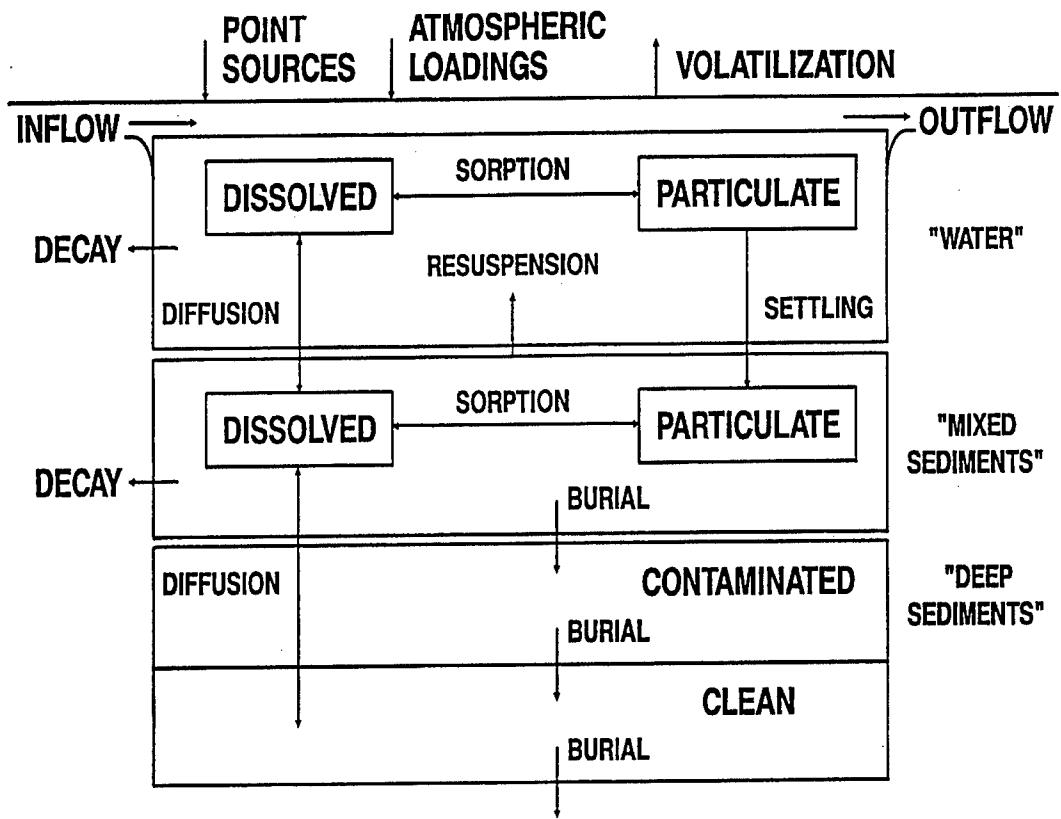


Figure 1. Schematic of processes

2 Numerical Model

Contaminant Mass Balances

For a well-mixed water column, the mass balance for a single contaminant in the water column can be written as

$$V_w \frac{dc_w}{dt} = Qc_i - Qc_w - k_w V_w c_w - k_v V_w c_w - v_s A_w F_{pw} c_w + v_r A_m c_m - v_d A_m (F_{dpm} c_m / \phi_m - F_{dw} c_w) + W \quad (1)$$

where V_w = volume of water body, m^3 ; c_w and c_m = concentrations of contaminant in water and mixed sediments, respectively, mg/m^3 ; c_i = inflow concentration of contaminant, mg/m^3 , which reflects both direct and tributary loadings; t = time, years; Q = flushing flow rate, m^3/year ; k_w = decay rate constant of the contaminant in the water, year^{-1} ; k_v = volatilization rate of contaminant, year^{-1} ; v_s = settling velocity of particulate matter, m/year ; A_w and A_m = surface areas of water and mixed sediment, respectively, m^2 ; F_{pw} = fraction of the total contaminant mass in the water in particulate form; v_r = resuspension velocity of sediments, m/year ; v_d = diffusion mass-transfer coefficient at the sediment-water interface, m/year ; F_{dpm} = fraction of the total contaminant mass in the mixed sediment layer dissolved in the pore water; F_{dw} = fraction of the total contaminant mass in the water in dissolved form; ϕ_m = porosity of the mixed layer; and W = external loads, kg/year . In the analysis in this report, it is assumed that the movement of one contaminant is independent of the presence of other contaminants. The term on the left-hand side of the equation represents contaminant accumulation in the water column. The first term after the equal sign represents the rate at which the contaminant is introduced into the water body. The second term represents the outflow rate of the contaminant by flushing flow. The third term is rate of contaminant decay, and the fourth term is the rate of contaminant mass volatilization. The next two terms are rate of contaminant transfer between the sediments in the water column and the mixed layer as a result of deposition and resuspension, respectively. The next term represents the net rates of contaminant transfer from between the water column and the mixed sediment. The last term in the equation is the rate of point source input.

To complete the representation of the interaction between contaminants in the water column and the mixed sediment layer, the contaminant mass balance in the mixed sediment is used and is written as

$$V_m \frac{dc_m}{dt} = -k_m V_m c_m + v_s A_w F_{pwc_w} - v_s A_m c_m - v_b A_m c_m + v_d A_m (F_{dw} c_w - F_{dpm} c_m / \phi_m) + v_d A_m (F_{dps} c_s(0) / \phi_s - F_{dpm} c_m / \phi_m) \quad (2)$$

where V_m = volume of mixed layer, m^3 ; k_m = the decay rate constant of the contaminant in the mixed layer, year^{-1} ; v_b = the burial velocity, m/year ; F_{dps} = fraction of the total contaminant mass in the deep sediment layer dissolved in the pore water; $c_s(0)$ = contaminant concentration at the top of the deep contaminated layer, mg/m^3 ; and ϕ_s = porosity of the deep sediment layer. In Equation 2, the term on the left-hand side of the equation represents the rate of contaminant mass accumulation in the mixed layer. The first term after the equal sign is the decay rate of the contaminant in the mixed layer. The next three terms represent the transfer of contaminants between the mixed layer and the water column and the deep sediment by settling, resuspension, and burial of sediment particles. The last two terms represent the interaction between the mixed layer and the water column and the deep sediment by diffusive transfer.

Coupling between the contaminants in the mixed sediment layer and the deep sediment takes place by diffusive transfer as well as by the burial of contaminated particles from the mixed sediment layer into the deep layer. Both the deep contaminated and clean sediments can be modeled with one-dimensional advection-diffusion-decay equations of the form

$$\frac{\partial c_s}{\partial t} = F_{dps} D_s \frac{\partial^2 c_s}{\partial z^2} - v_b \frac{\partial c_s}{\partial z} - k_s c_s \quad (3)$$

where c_s = the contaminant concentration in the deep sediments mg/m^3 ; D_s = diffusion rate in the sediment pore water, m^2/year ; z = depth into the sediment, m , where $z = 0$ at the top of the deep sediments; and k_s = the decay rate constant of the contaminant in the deep sediments, year^{-1} . The term on the left-hand side of the equation is the rate of contaminant concentration change in the sediment. The first term after the equal sign is the rate of contaminant transfer by diffusion in the sediment pore water. The second term represents the rate of contaminant transfer due to sediment particle burial, and the last term represents the decay rate of contaminants in the pore water of the deep sediment.

Solids Budget

In addition to the contaminant mass, the sediment mass must be conserved. The velocity terms v_s , v_r , and v_b in Equations 1 and 2 are computed according to a steady-state mass balance for mixed-sediment layer solids by Chapra and Reckhow (1983). The mass balance is

$$\theta = v_s A_w s_w - (v_r + v_b) A_m (1 - \phi_s) \rho_p \quad (4)$$

where ρ_p = the density of the sediment particles, gm/m^3 . The framework assumes that suspended solids concentration, s_w , is given. Therefore, if two of the three velocities are specified, Equation 4 can be employed to calculate the third.

In addition to these transfer velocities, the other facet of the physical system is the sediment porosity. Different porosities may occur in the mixed layer and the deep sediments. Within the layers of the deep sediment region, porosity can vary from layer to layer, but is assumed constant over time. This means that compaction is not included. The same argument is assumed for particle density.

Parameter Estimation

The F variables in Equations 1–3 are dimensionless ratios that reflect how the contaminant partitions between solid matter and water assuming a linear sorption mechanism. Denoting the contaminant as A , the fraction of the total mass of contaminant A in the water column in particulate form is:

$$F_{pw} = \frac{\text{Mass of } A(\text{Particulate Form})}{\text{Mass of } A(\text{Dissolved Form}) + \text{Mass of } A(\text{Particulate Form})} = \frac{K_{dw} s_w}{1 + K_{dw} s_w} \quad (5)$$

and in dissolved form is $1-F_{pw}$:

$$F_{dw} = \frac{\text{Mass of } A(\text{Dissolved Form})}{\text{Mass of } A(\text{Dissolved Form}) + \text{Mass of } A(\text{Particulate Form})} = \frac{1}{1 + K_{dw} s_w} \quad (6)$$

The fraction of the total mass of contaminant A in the mixed/deep sediment layer that is in the pore water in dissolved form, F_{dp} , is:

$$F_{dp} = \frac{\text{Mass of } A(\text{Dissolved Form})}{\text{Mass of } A(\text{Dissolved Form}) + \text{Mass of } A(\text{Particulate Form})} = \frac{\phi}{\phi + K_{ds}(1 - \phi)\rho_p} \quad (7)$$

where K_{dw} and K_{ds} = the contaminant partitioning coefficient in the water and mixed/deep sediments, respectively, m^3/g ; s_w = suspended solids concentration in the water, g/m^3 ; and ϕ is the porosity of the mixed/sediment layer. Note that the model allows different values of this parameter to be employed in the mixed layer and the vertically segmented sediments (F_{dpm} and F_{dps}).

The decay rate constants, k_w , k_m , and k_s , represent all mechanisms for decay except volatilization, which is accounted for separately. These mechanisms include photolysis, hydrolysis, and bacterial degradation. The mass transfer coefficient for diffusive sediment–water exchange is related to more fundamental parameters by

$$v_d = \frac{\phi D_s}{z'} \quad (8)$$

where z' = characteristic length over which the gradient exists at the sediment–water interface, m. Note that a value of 1 cm is assumed for z' after Thomann and Mueller (1987). Also, D_s is related to molecular diffusivity, D_m , by the relation (Berner 1980, Manheim and Waterman 1974)

$$D_s = D_m \phi^2 \quad (9)$$

Volatilization rate

The volatilization rate, k_v , in year⁻¹, is computed by

$$k_v = F_{dw} \frac{v_v}{z_w} \quad (10)$$

where v_v = a volatilization transfer coefficient, m/year, and z_w = depth of the water column, m. The volatilization transfer coefficient can be computed according to the Whitman two-film theory as

$$v_v = \frac{K_l K_g H_e}{K_g H_e + K_l} \quad (11)$$

where H_e = a dimensionless Henry's coefficient which is related to the common form, He' , in atm m³/mole, by

$$H_e = \frac{H_e'}{RT} \quad (12)$$

where R = the universal gas constant = 8.206×10^{-5} atm m³/(mole °K), and T = absolute temperature, °K. A temperature of 298 °K (25°C) is assumed in the model. The parameter K_g is a gas-film mass transfer coefficient, m/year, which can be related to wind speed, U_w , m/s, and molecular weight, MW , g/gmole, by Mills et al. (1982),

$$K_g = 61320 \left(\frac{18}{MW} \right)^{0.25} U_w \quad (13)$$

The parameter K_l is a liquid-film mass transfer coefficient, m/year, which can be related to wind speed, U_w , m/s, and molecular weight, MW , g/gmole, by (Mills et al. 1982, Banks 1975, Banks and Herrera 1977)

$$K_l = 356 \left(\frac{32}{MW} \right)^{0.25} (0.728U_w^{0.5} - 0.317U_w + 0.0372U_w^2) \quad (14)$$

Partitioning coefficient

The partitioning coefficient for organic contaminants is computed via (Karickhoff, Brown, and Scott 1979)

$$K_d = 0.617 f_{oc} K_{ow} \quad (15)$$

where K_d = equilibrium partitioning coefficient, L/kg, f_{oc} = the weight fraction of organic carbon in the solid matter, g-orgC/g, and K_{ow} = octanol-water partitioning coefficient, (mg/m³-octanol)/(mg/m³-water). Note that the model assumes a default of 0.05 for f_{oc} . Different values for f_{oc} are allowed for the water column, mixed layer, and the deep sediments. Analogous to other physico-chemical characteristics of the sediments, the f_{oc} can vary with depth (layers) in the deep sediments.

Numerical Solution

The coupled set of differential equations is solved numerically. The two first-order ordinary differential equations are solved using an adaptive-step-size, fourth-order Runge-Kutta method. The partial differential equation is solved using the Crank-Nicholson technique.

The solution presented here assumes a well-mixed water column and sediment column with the concentration in both being constant. The initial condition for Equation 1 at $t = 0$ is $c_w = c_{wo} = \text{constant}$, and the initial condition for Equation 2 at $t = 0$ is $c_m = c_{mo} = \text{constant}$. The initial conditions at $t = 0$ for Equation 3 are

$$\begin{array}{lll} c_s = c_{so} & \text{for} & z_m < z < L \\ c_s = 0 & \text{for} & L < z < \infty \end{array}$$

and the boundary conditions are

$$\begin{aligned} \text{at } z = z_m, \quad J &= J_{ms} \\ \text{at } z = \infty, \quad \frac{dc_s}{dz} &= 0 \end{aligned}$$

where L = distance from the top of the mixed layer to the bottom of the contaminated layer, m; J = mass flux of the contaminant, g/m²-year; and J_{ms} = mass flux of the contaminant from the mixed layer to the sediment layer, g/m²-year.

3 Verification

Model Verification With Analytical Solution

Chapra (1997) presents an analytical solution to Equations 1 and 2. The solution is based on the Laplace transform of the differential equations. This solution does not account for the deep sediment layer in which contaminant flux is controlled by diffusion. In order to compare the numerical solution of Equations 1 and 2 with the analytical solution presented in Chapra (1997), only the top two layers, a water layer and a mixed sediment layer, are used for the simulation. Obviously, since the model presented in this report includes a deep sediment layer, the effect of this layer on the contaminant mass in the water and mixed sediment must be assessed. The data used for this comparison are shown in Table 1.

The first comparison is shown in Figure 2, which is a plot of the time variation of contaminant concentration in the water column. The solid line represents the analytical solution, while the other lines represent the numerical simulation for a deep sediment layer with the same contaminant concentration as the mixed layer and with zero concentration of contaminants. For the case when the deep sediment layer has the same concentration as the mixed layer, the flux of contaminants between these two layers will not affect the contaminant concentration in the water column at the initial stage but will show the impact after some time due to the flux of contaminants between the mixed layer and the deep sediment layer. In this case, contaminant loss from the mixed layer to the underlying sediment by diffusion is reduced due to the small concentration gradient between these layers; hence, more contaminant mass is available for interaction with overlying water column. This is evident in Figure 2, which shows that the numerical model predicts higher concentrations after several years of simulation. The third line shown in Figure 2 is for the case when the concentration of contaminants in the deep sediment is zero. This situation will cause a flux of contaminants from the mixed layer into the underlying sediment layer causing less contaminant mass in the mixed layer to be available for interaction with the water column. After several years of simulation, contaminant mass in the mixed layer and in the deep sediment continues to provide contaminants for interaction with the water column. This is evident in the slightly larger concentration of contaminants predicted by the numerical model after a long time of simulation.

Figure 3 shows the contaminant mass in the mixed layer as predicted by the analytical model and the numerical model for the same concentrations as discussed above. The impact of the presence of the deep sediment can be explained as above.

Table 1. Values Used in the Comparison of RECOVERY

Parameter	Value
Water Column	
Flow through (m ³ /year)	2x10 ⁷
Surface area (m ²)	1x10 ⁷
Depth (m)	10
Suspended sediment concentration (g/m ³)	5
Weight fraction of contaminant in solid	0.05
Initial contaminant concentration (μg/m ³)	0
Mixed Layer	
Thickness (cm)	5
Surface area (m ²)	1x10 ⁷
Porosity	0.7
Weight fraction of contaminant in solid	0.05
Initial contaminant concentration (μg/m ³)	1000
Sediment Layer	
Thickness (m) AV	1
Porosity	0.7
Weight fraction of contaminant in solid	0.05
Initial contaminant concentration (μg/m ³)	0 & 1000
Sediment Properties	
Density in mixed layer (g/m ³)	2.5x10 ⁶
Density in sediment layer (g/m ³)	2.5x10 ⁶
Settling velocity (m/year)	90
Burial velocity (m/year)	0.0005
Compound Properties	
Molecular diffusivity (cm ² /sec)	5x10 ⁻⁶
Decay coefficient: particulate in water (year ⁻¹)	0
Decay coefficient: dissolved in water (year ⁻¹)	0
Decay coefficient: particulate in mixed layer (year ⁻¹)	0
Decay coefficient: dissolved in mixed layer (year ⁻¹)	0
Decay coefficient: particulate in deep sediment (year ⁻¹)	0
Decay coefficient: dissolved in deep sediment (year ⁻¹)	0
Henry's constant (atm-m ³ /gmole)	3.9x10 ⁻⁵
Octanol-water partitioning coef. (mg/m ³ -octanol/mg/m ³ -water)	1x10 ⁵
Molecular weight (g/gmole)	354.5

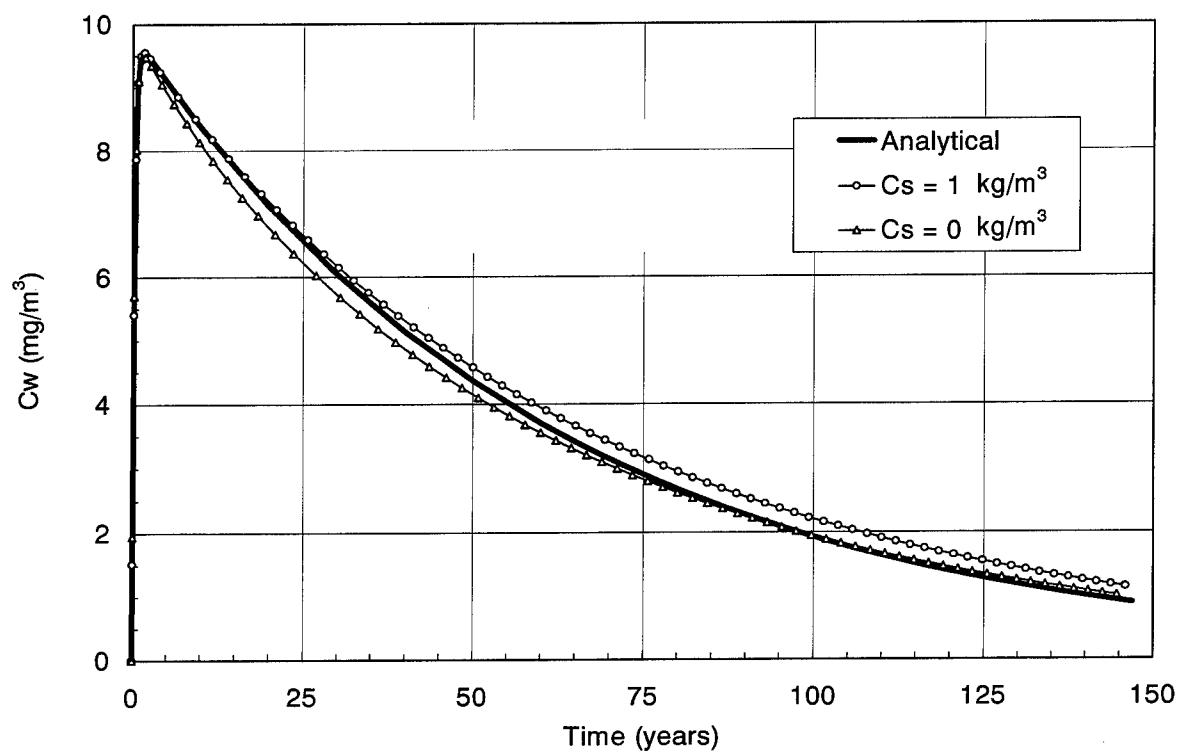


Figure 2. Comparison of contaminant concentration in the water column

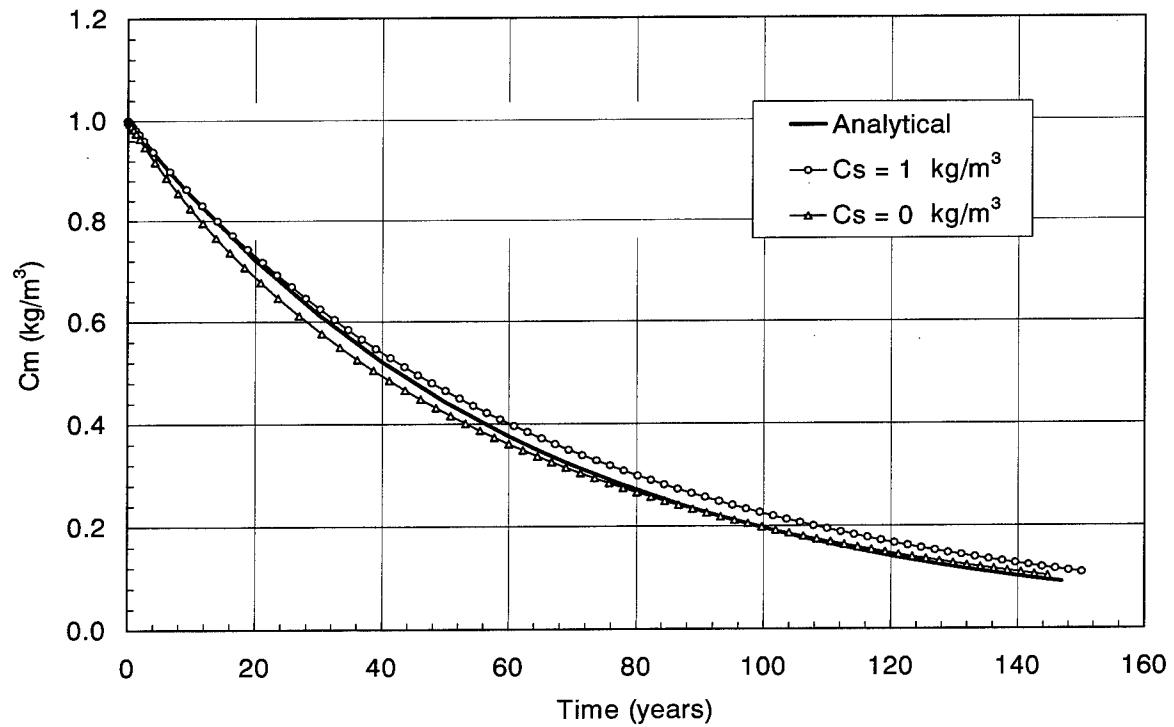


Figure 3. Comparison of contaminant concentration in the mixed layer

Model Verification with Laboratory Data

Model simulations were compared to short-term laboratory experimental data to evaluate the accuracy and the applicability of the model in predicting desorption, diffusion, and degradation kinetics. In the experimental phase, radio-labelled naphthalene was selected as a tracer to determine the rate and magnitude of contaminant mobilization from Wayne County, Indiana, reservoir sediment. Data from the experimental phase were used to verify and assess the accuracy of the model in predicting desorption and degradation. The model was modified to be more applicable to laboratory microcosm settings and short-term scenarios (7 days).

To compare the laboratory results with simulation results of RECOVERY, several decay coefficients were tested to determine the value that best fits the data. These values were based on half-life values from field data reported by Howard et al. (1991) in which naphthalene's half-life varied from 12 to 480 hr. For a slow decay rate corresponding to a half-life of 480 hr, naphthalene desorption did not compare favorably with experimental data shown in Figure 4. The model tended to overpredict naphthalene desorption and kinetic trends. The predicted desorption kinetics exhibited a slow and steady increase that reached equilibrium between days 3 and 7, at approximately 5.5 mg/m³. On the other hand, the experimental data showed that equilibrium was reached within 24 hr at approximately 2.2 mg/m³. This indicated that naphthalene in the sample decays faster, i.e., its half-life is smaller than 480 hr. Several half-life values were used, and the results indicated that a half-life of 48 hr best represents the decay trends exhibited in the laboratory.

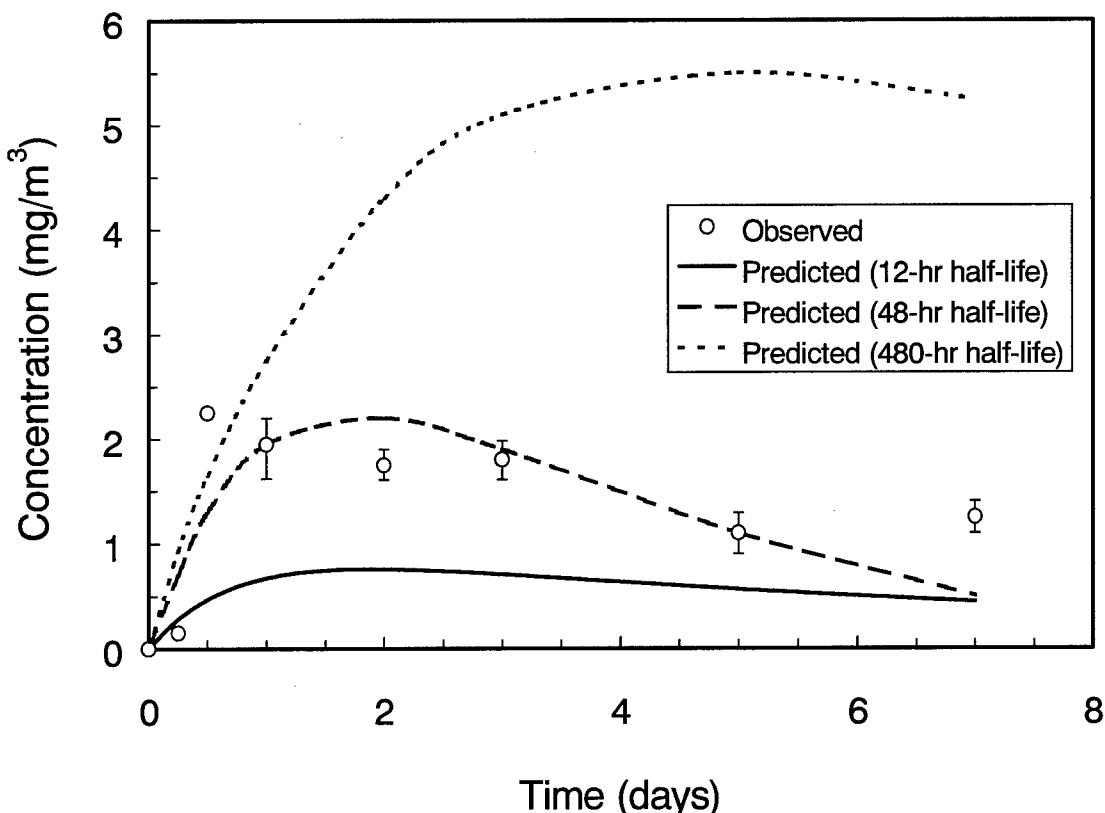


Figure 4. Naphthalene concentrations in the aqueous phase

Field Verification

The RECOVERY model was applied to analyze a field-scale experiment in which a flooded limestone quarry was dosed with equal quantities of the insecticides DDE and lindane. The same experiment was previously analyzed with a time variable model by Di Toro and Paquin (1983) with good results.

The study was conducted in two flooded limestone quarries located near the town of Oolitic in Bedford County, Indiana. The quarries were allowed to flood naturally for 5 years before being dosed with lindane and DDE. One quarry was experimentally dosed (quarry T), and the second was used as the control (quarry C) (Waybrant 1973). Quarry T was 300 ft (91.4 m) long, 135 ft (41.1 m) wide, and an average of 50 ft (15.2 m) deep. Quarry T was the smaller of the two in area with extremely clear water and a generally flat bottom. The average Secchi disc reading for quarries C and T was 20 ft (6.1 m). Both quarries exhibited thermal stratification from March to November.

The relatively soft and slightly alkaline water found in the quarries tends to indicate that the quarries received very little groundwater (Waybrant 1973). The water chemistry and physical characteristics of the quarries indicated that the quarries were primarily filled with rainwater and runoff water which did not percolate through the limestone to the groundwater.

The bottom material in quarry T was made up of 3 to 5 cm of fine brownish gyttja underlaid by a white inorganic mixture of limestone dust and silica sand (Waybrant 1973). In general, the top sediment layers were aerobic. The mud layer contained on the average 1 percent sand, 42 percent silt, and 57 percent clay.

Quarry T was treated with lindane and DDE at a concentration of 0.2 mg/m³ to the epilimnion or 0.05 mg/m³ overall (2.7764 g of DDE and 2.7752 g of lindane) (Waybrant 1973). The quarries were analyzed after the treatment, and the results showed that essentially all of the insecticides were initially released in the epilimnion. The quarries were periodically sampled, and the results are presented in Table 2. Both water and bottom sediments were analyzed for DDE and lindane. The results for insecticides in the bottom sediment material are shown in Table 3.

The concentration of DDE and lindane remaining in the water column after 5 days differed significantly (Table 2), showing different transport mechanisms by the two insecticides. After day 1 a significant runoff event occurred in quarry T, washing a significant amount of sediment into the quarry. The suspended sediment load caused the DDE concentration in the water column to decrease as suspended solids and the adsorbed DDE settled to the lake bottom. DDE hydrophobic properties cause affinity to suspended solids and organic matter, while lindane, a more polar compound, tends to have higher affinity for water.

Over the sampling period an extremely rapid distribution of DDE in the water column was noted as opposed to an 87-percent retention of lindane in the surface layers (Waybrant 1973). The quarry underwent turnover at day 144, when the DDE and lindane distribution in the water column was essentially homogeneous (Table 2). The lindane concentration in the water column decreased until day 123, after which the insecticide concentration remained constant until the sample after the following spring.

DDE and lindane were both detected in the bottom sediments at significantly higher concentrations after the initial pesticide loading. However, the ultimate fates of both pesticides were considerably different. DDE, a more hydrophobic compound, was rapidly deposited in the bottom sediments (Table 3), while lindane concentration never reached the relatively high levels observed with DDE.

DDE peaked at 35 mg/m³ in the bottom sediments, while lindane levels did not exceed 2.5 mg/m³ in the sediments. Both compounds reached the highest level in the sediments between day 81 and day 123 with lindane penetrating the lower depth of the bottom sediments while DDE remained mostly on the top layer.

Table 2. Concentrations of DDE and Lindane in the Water Column

Sampling Day	DDE, $\mu\text{g}/\text{m}^3$ $X \pm \text{SD}$	Lindane, $\mu\text{g}/\text{m}^3$ $X \pm \text{SD}$
1	44.420 ± 16.336	47.270 ± 3.676
5	14.994 ± 3.429	62.792 ± 10.419
10	4.270 ± 2.066	60.828 ± 2.733
21	3.520 ± 1.768	58.874 ± 15.683
42	3.311 ± 1.324	50.418 ± 2.087
60	2.132 ± 0.613	29.852 ± 16.510
81	2.006 ± 0.163	32.939 ± 4.048
102	1.466 ± 0.163	34.577 ± 4.059
123	0.988 ± 0.220	25.440 ± 7.369
144	0.789 ± 0.171	23.189 ± 2.378
173	0.958 ± 0.163	21.318 ± 0.667
242	0.952 ± 0.103	20.284 ± 1.458

Note: SD = standard deviation, X = mean (Waybrant 1973).

Some important notes from the flooded quarry experiment were the significantly higher water column concentration of lindane, an order of magnitude above DDE at the end of the study; the significantly lower sediment concentration of lindane than of DDE, with lindane penetrating to the deeper sediment layer of 3.5 to 5.5 cm; and the nonexistence of a pronounced vertical lindane concentration gradient in the sediment profile.

Approximately 5 years after the initial dosing of the quarry, on June 21, 1977, several sediment samples were collected and analyzed for DDE (Di Toro and Paquin 1983). The DDE concentration measured in that sampling event ranged from 3.4 to 11.2 mg/m^3 for one sample and from 2.9 to 4.2 mg/m^3 for another. The water column was sampled at the same time, but the detection limit of the analysis was 30 $\mu\text{g}/\text{m}^3$ (Di Toro and Paquin 1983). The 1977 samples were not analyzed for lindane.

Rate coefficients

To simulate the flooded quarry with the RECOVERY model, the basic assumptions of the model need to be satisfied. The first assumption, the water body is well-mixed, might be satisfied after day 123 (Table 2) and definitely at day 144. For the application of RECOVERY, the simulation was performed from days 81 and 123, a time where the pesticide profile seems fairly uniform. The sediments are the only source of the contaminant to the water body at day 81 for DDE and day 123 for lindane. At those days the concentration in the sediment peaks for each of the simulated compounds. Once the concentration peaks in the sediment, the water can no longer be a source of contaminant (quasi-equilibrium is temporarily established) unless a considerable loss of contaminant is occurring in the sediments.

Table 3. Concentrations of DDE and Lindane in the Bottom Sediments

Day	Depth, cm	DDE, mg/m ³		Lindane, mg/m ³	
		X ± SD	% of Total	X ± SD	% of Total
1	1.5	0.1		7.05	
	3.5			7.05	
	5.5				
5	1.5	18.66 ± 14.50	30.27	1.54 ± 0.14	2.50
	3.5				
	5.5				
10	1.5	22.28 ± 6.04	36.15	1.48	2.40
	3.5	1.15 ± 1.49	1.87	<0.05	
	5.5	<0.10		<0.05	
21	1.5	12.73 ± 11.30	20.65	1.64 ± 0.43	2.65
	3.5	0.28 ± 0.11	0.45	1.04 ± 0.87	
	5.5				
42	1.5	20.84 ± 5.53	33.82	0.98 ± 1.36	1.59
	3.5	0.14	0.23		
	5.5	<0.1		<0.05	
81	1.5	35.30 ± 27.45	57.27	1.13 ± 1.52	1.83
	3.5	<0.10		0.99	
	5.5	<0.10		0.95 ± 0.57	
123	1.5	27.27 ± 15.85	45.24	1.87 ± 1.77	3.03
	3.5	0.11	0.18	2.46 ± 2.31	3.99
	5.5	0.88 ± 1.06	1.43	1.40 ± 0.97	2.64
173	1.5	30.92 ± 13.39	50.17	1.78 ± 1.60	2.88
	3.5	5.08	8.24	2.15	3.49
	5.5	0.18		<0.05	
242	1.5	19.69 ± 2.80	31.95	<0.05	
	3.5	0.31 ± 0.02	0.50	<0.05	
	5.5	0.39 ± 0.45			

Note: SD = standard deviation, X = mean (Waybrant 1973).

The initial concentration of the compound in the contaminated region is uniform throughout that region after days 81 and 123. The sediments are uniform, within the analytical measurements, and in the deeper sediments the concentration varies in the vertical direction only. Therefore, the RECOVERY simulations started, time = 0, at day 81 for DDE and day 123 for lindane.

Initial water concentration for lindane was set to $25.4 \mu\text{g}/\text{m}^3$ and $3.5 \mu\text{g}/\text{m}^3$ for DDE. The initial sediment concentration was set to $35.3 \mu\text{g}/\text{m}^3$ for DDE and $1.87 \mu\text{g}/\text{m}^3$ for lindane. Within the analytical precision of the data and the collection scheme, the above values seem to be representative of the initial conditions for the quarry exposure. The inflow to the quarry was estimated to be insignificant in comparison to the overall volume of water in the quarry (Di Toro and Paquin 1983). The water depth in the quarry was 13.9 m, and the quarry contained $5.23 \times 10^4 \text{ m}^3$ of water (Waybrant 1973).

The depth of the mixed sediment layer was set to 1.0 cm for DDE and 3.0 for lindane, since DDE was not detected at substantial levels below 1.5 cm. In this case, the depth of the deep contaminated sediments was set to the allowable minimum, which was 0.05 m (0.06 m for the lindane run) below which RECOVERY can become unstable. Suspended solids were set to 5 mg/L based on an analysis by Di Toro and Paquin (1983) on Secchi disc readings and sediment trap data. Resuspension was set to zero, the burial velocity was set to $5.0 \times 10^{-4} \text{ m/year}$, and the settling velocity was estimated from the solids mass balance in RECOVERY. The estimated value was 87.5 m/year. Both the settling velocity and the burial velocity were within the range reported by Chapra (1982).

The partitioning coefficient for DDE was computed as 154,000 L/kg based on an assumed organic content of 0.05 (weight fraction) and an octanol/water partitioning coefficient of $5 \times 10^4 \text{ (mg/m}^3\text{--octanol)}/(\text{mg/m}^3\text{--water})$. The molecular diffusivity was set to the default of $5 \times 10^{-6} \text{ cm}^2/\text{sec}$, the calculated volatilization rate for DDE was 5.09 per year, and the degradation rate was set to zero for DDE (half-life of 15 years (Howard et al. 1991)).

For lindane the volatilization rate was 6.62×10^{-2} per year, and the degradation rate was set to 0.9 per year in both the water column and the sediments. The degradation rate agrees with the value of 0.0025/day used by Di Toro and Paquin (1983) in their application.

Simulation results

The physical and chemical parameters estimated and selected in the previous section were used in the simulation of DDE and lindane in a flooded limestone quarry. Results from the initial experiment and follow-up work were used to compare against the simulation from RECOVERY.

The simulated and observed lindane distributions are shown in Figures 5 and 6 for water and bottom sediments, respectively. Lindane decreases from $25 \mu\text{g}/\text{m}^3$ to less than $1 \mu\text{g}/\text{m}^3$ after 5 years in the water column. Lindane in the sediment decreases from $1.87 \mu\text{g}/\text{m}^3$ to below $1 \mu\text{g}/\text{m}^3$ after 5 years.

Figures 7 and 8 show the DDE concentration in the water column and sediment bed, respectively. Initially DDE was transferred to the sediment bed by deposition of suspended sediment contaminated with DDE from the quarry initial application. After the initial loading to the bed, the process reverses once the water column concentration starts decreasing because of the loss of DDE by volatilization. At this point the sediment bed becomes the source of DDE for the water column; since there is no degradation in the bed, the only removal mechanism is volatilization. Contrary to lindane, where the pesticide was mostly in the water column, DDE is mostly in the bed; thus, it takes longer to clean the bed than it does to clean the water. If degradation in the sediment bed were significant, then a much faster cleanup would occur.

DDE in the water column after 5 years agrees very well with Di Toro's (Di Toro and Paquin 1983) prediction of less than $1 \mu\text{g}/\text{m}^3$ (Figure 7). In the sediment, the simulation (Figure 8) shows

good agreement with the field data, but a little higher than Di Toro's result of 5.6 mg/m³ (Di Toro and Paquin 1983). However, both models predict a sediment concentration after 10 years of approximately 1 mg/m³. Figures 9 and 10 present a second simulation of DDE in the water and sediment bed, respectively. Porosity in the mixed bed was increased to 0.8 and the degradation of DDE in the water was set to 3.0 per year to account for photodegradation of DDE. The value of 3.0/year is similar to the one used by Di Toro, 0.013/day (4.75/year) (Di Toro and Paquin 1983). This simulation agrees more closely with the other model results and shows remarkable agreement with the field data, with the exception of spring sampling.

Overall, the simulation of DDE and lindane in the flooded limestone quarry was simulated with confidence using the model RECOVERY. The confirmation application was performed with minimum calibration. In addition, very few data were needed to accomplish the task.

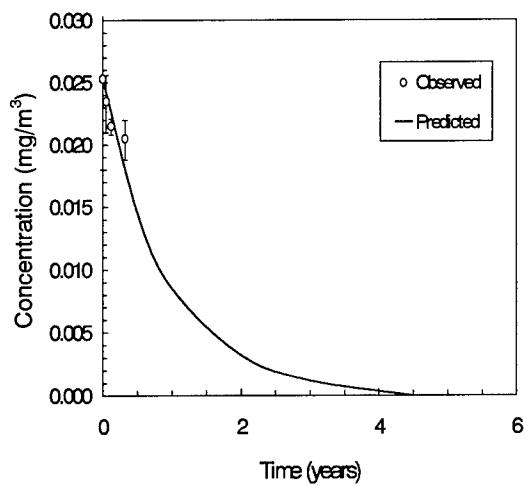


Figure 5. Lindane concentration in water

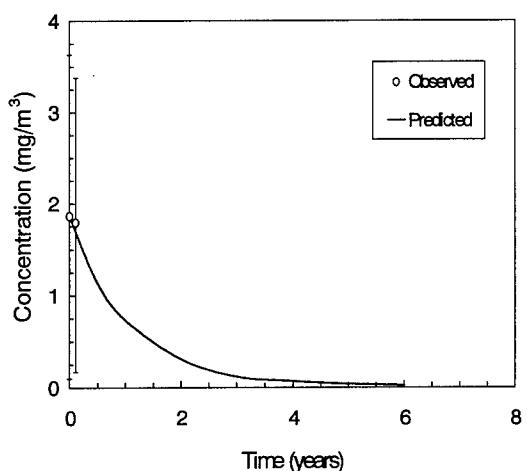


Figure 6. Lindane concentration in mixed sediment

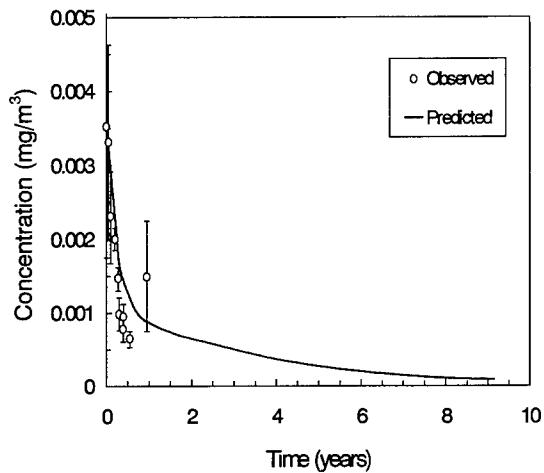


Figure 7. DDE concentration in water

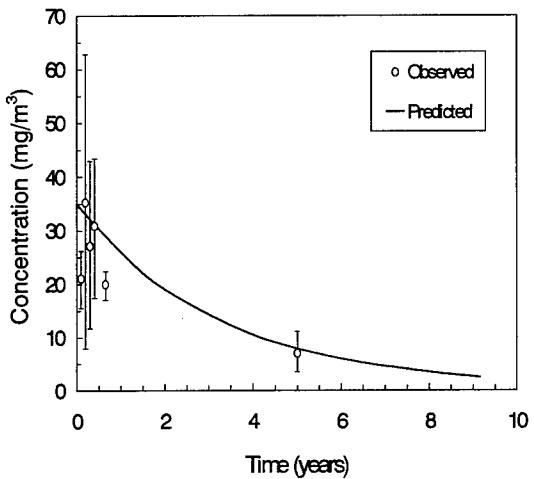


Figure 8. DDE concentration in mixed sediment

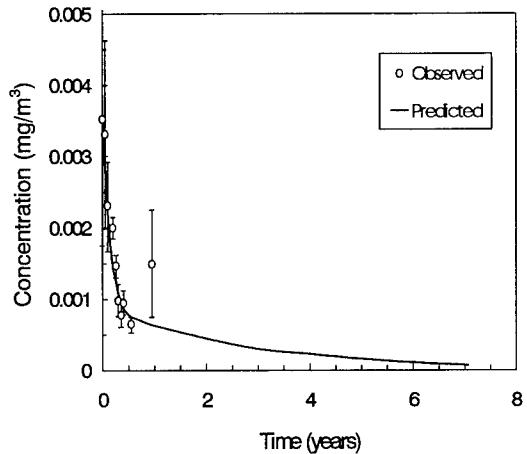


Figure 9. Final DDE concentration in water

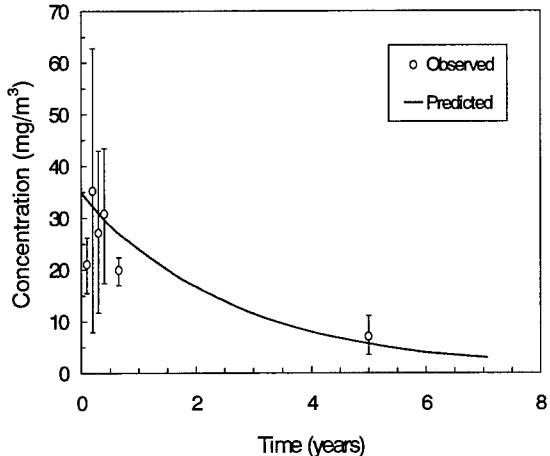


Figure 10. Final DDE concentration in mixed sediment

4 Conclusions

The model described herein allows for a rapid analysis of recovery scenarios for contaminated sediments and cap evaluations. The model can be applied in a variety of situations including lakes, embankments, harbors, estuaries, and ocean parcels as long as the assumption of a completely mixed water body is acceptable along with the other model assumptions. Average yearly flushing would be needed in any of the applications above, in addition to the other chemical and physical parameters for a well-defined simulation.

The model was verified against laboratory and field experiments. The confirmation shows the ability of the program to simulate behavior of organics in a real system with a limited amount of data. Results are similar to those predicted by another model and thus appear to demonstrate the validity of the algorithms used to describe the fate and transport of organics.

The RECOVERY model was limited to measurable system parameters, based on known physical and chemical processes. Plots generated by the model provided a reasonable fit to the experimental data, with few exceptions. In instances where the model did not estimate desorption values, trends that were similar to those observed in the experimental data were predicted.

The RECOVERY model can be used to predict contaminant desorption. Incorporating easily measured or estimated parameters in the model enhanced and improved the capability for predicting desorption of contaminants from sediments.

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Appendix A

Notation

A_w = surface area of water, m^2 ;

A_m = surface area of mixed sediment, m^2 ;

c_i = inflow concentration, mg/m^3 ;

c_m = concentration of contaminant in mixed sediments, mg/m^3 ;

c_{mo} = initial concentration of contaminant in mixed sediments, mg/m^3 ;

c_s = contaminant concentration in the deep sediments, mg/m^3 ;

c_{so} = initial contaminant concentration in the deep sediments, mg/m^3 ;

$c_s(0)$ = contaminant concentration at the top of the deep contaminated layer, mg/m^3 ;

c_w = concentration of contaminant in water, mg/m^3 ;

c_{wo} = initial concentration of contaminant in water, mg/m^3 ;

D_m = molecular diffusivity in the sediment pore water, m^2/year ;

D_s = diffusion rate in the sediment pore water, m^2/year ;

f_{oc} = weight fraction of organic carbon in the solid matter, $\text{g-}\text{orgC}/\text{g}$;

F_{dp} = fraction of contaminant mass in sediment dissolved in the pore water, dimensionless;

F_{dpm} = fraction of contaminant mass in mixed sediment layer dissolved in the pore water, dimensionless;

F_{dps} = fraction of contaminant mass in deep sediment layer dissolved in the pore water, dimensionless;

F_{dw} = fraction of contaminant in the water column in dissolved form, dimensionless;

F_{pw} = fraction of contaminant in the water column in particulate form, dimensionless;

H_e = Henry's coefficient, dimensionless;

He' = Henry's coefficient, $\text{atm m}^3/\text{mole}$;

J = mass flux of the contaminant, $\text{g}/\text{m}^2\text{-year}$;

J_{ms} = mass flux of the contaminant from the mixed layer to the sediment layer, $\text{g}/\text{m}^2\text{-year}$;

k_m = decay rate constant of the contaminant in the mixed layer, year^{-1} ;

k_s = decay rate constant of the contaminant in the deep sediments, year⁻¹;
 k_v = volatilization rate of contaminant, year⁻¹;
 k_w = decay rate constant of the contaminant in the water, year⁻¹;
 K_d = equilibrium partitioning coefficient, L/kg;
 K_{ds} = contaminant partitioning coefficient in the sediment, m³/g;
 K_{dw} = contaminant partitioning coefficient in the water, m³/g;
 K_g = gas-film mass transfer coefficient, m/year;
 K_l = liquid-film mass transfer coefficient, m/year;
 K_{ow} = octanol-water partitioning coefficient, (mg/m³-octanol)/(mg/m³-water);
 L = distance from top of the mixed layer to bottom of the contaminated layer, m;
 MW = molecular weight, g/gmole;
 Q = flushing flow rate, m³/year;
 R = universal gas constant, atm m³/(mole °K);
 s_w = suspended solids concentration in the water, g/m³;
 t = time, years;
 T = absolute temperature, °K;
 U_w = wind speed, m/s;
 v_b = burial velocity, m/year;
 v_d = diffusion mass-transfer coefficient at the sediment-water interface, m/year;
 v_r = resuspension velocity of sediments, m/year;
 v_s = settling velocity of particulate matter, m/year;
 v_v = volatilization transfer coefficient, m/year;
 V_m = volume of mixed layer, m³;
 V_w = volume of water body, m³;
 W = external loads, kg/year;
 z = depth into the sediment, m;
 z' = characteristic length over which the concentration gradient exists at the sediment-water interface, m;
 z_m = thickness of mixed layer, cm;
 z_w = depth of water column, m;
 ϕ = sediment porosity, dimensionless;
 ϕ_m = mixed sediment layer porosity, dimensionless;
 ϕ_s = deep sediment layer porosity, dimensionless; and
 ρ_p = density of sediment particles, g/m³.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) This report describes a screening-level model (RECOVERY) used to assess the long-term impact of contaminated bottom sediments on surface waters. The model couples contaminated interaction between the water column and the bottom sediment, as well as between the contaminated and clean bottom sediments. The analysis is intended primarily for organic contaminants with the assumption that the water column is well mixed. The contaminant is assumed to follow linear, reversible, equilibrium sorption and first-order decay kinetics. The physical representation of a system consists of a well-mixed water column (i.e., zero-dimensional) underlain by a vertically stratified sediment column (i.e., one-dimensional). The sediment is well-mixed horizontally but segmented vertically into a well-mixed surface (active) layer and deep sediment. The deep sediment is segmented into variably contaminated and clean sediment regions. Processes incorporated in the model are sorption, decay, volatilization, burial, resuspension, settling, bioturbation, and pore-water diffusion. The solution couples contaminant mass balance in the water column and in the mixed sediment layer along with diffusion in the deep sediment layers. The model was verified against laboratory and field data, as well as against an analytical solution for the water and mixed sediment layers. These comparisons indicate that the model can be used as an assessment tool for evaluating remediation alternatives for contaminated bottom sediments.			
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